

AD-A117 890

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DISSOCIATIVE ADSORPTION OF CO<sub>2</sub> ON OXIDIZED AND REDUCED PT/TIO<sub>2</sub>. (U)

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OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0922

Task No. NR 056-578

TECHNICAL REPORT NO. 25

Dissociative Adsorption of  $\text{CO}_2$  on Oxidized and Reduced  $\text{Pt/TiO}_2$

by

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Prepared for publication

in

Journal of Physical Chemistry

Department of Chemistry

University of Texas at Austin

Austin, Texas 78712

July, 1982

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-411789C	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Dissociative Adsorption of CO <sub>2</sub> on Oxidized and Reduced Pt/TiO <sub>2</sub>		5. TYPE OF REPORT & PERIOD COVERED Technical Report 25 Jan. 1 - Dec. 31, 1982
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Katsumi Tanaka and J. M. White		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0922
9. PERFORMING ORGANIZATION NAME AND ADDRESS J. M. White Dept. of Chemistry, University of Texas Austin, TX 78712		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project NR-056-578
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, VA 22217		12. REPORT DATE July 23, 1982
		13. NUMBER OF PAGES 17
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Preprint; Journal of Physical Chemistry (in press)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) On both oxidized and reduced Pt/TiO <sub>2</sub> , carbon dioxide decomposes at room temperature to form chemisorbed oxygen atoms and carbon monoxide. In the absence of Pt, no decomposition was found. On reduced samples, the oxygen atoms were stabilized on the titania support and reacted further with CO <sub>2</sub> to form adsorbed bidentate carbonate. On reduced Pt/TiO <sub>2</sub> , the adsorbed CO produced in the decomposition reaction produced a linearly bound species at step sites in the initial stages of the reaction. As the reaction proceeded, CO adsorbed linearly on terrace sites was found. On oxidized Pt/TiO <sub>2</sub> , the decomposition rate was much slower		

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*J. Phys. Chem.*  
(in press).

Dissociative Adsorption of  $\text{CO}_2$  on  
Oxidized and Reduced  $\text{Pt/TiO}_2$  (a)

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ABSTRACT

On both oxidized and reduced  $\text{Pt/TiO}_2$ , carbon dioxide decomposes at room temperature to form chemisorbed oxygen atoms and carbon monoxide. In the absence of Pt no decomposition was found. On reduced samples, the oxygen atoms were stabilized on the titania support and reacted further with  $\text{CO}_2$  to form adsorbed bidentate carbonate. On reduced  $\text{Pt/TiO}_2$ , the adsorbed CO produced in the decomposition reaction produced a linearly bound species at step sites in the initial stages of the reaction. As the reaction proceeded, CO adsorbed linearly on terrace sites was found. On oxidized  $\text{Pt/TiO}_2$ , the decomposition rate was much slower and only linear step site species were observed. From the results we conclude that Pt step sites are the active sites for  $\text{CO}_2$  dissociation.

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## 1. Introduction.

Since the discovery by Primet et al.<sup>(1)</sup> of frequencies associated to adsorbed CO after exposure of Rh/Al<sub>2</sub>O<sub>3</sub> catalysts to CO<sub>2</sub>, many papers have been published dealing with the interaction of CO<sub>2</sub> with Rh-based catalysts. Schorjail et al.<sup>(2-4)</sup> studied CO<sub>2</sub> adsorption on several Rh single crystal and polycrystalline samples and found evidence for dissociation of CO<sub>2</sub> using electron energy loss vibrational spectra. However, several other groups find no evidence for dissociated CO<sub>2</sub> on Rh.<sup>(5-7)</sup> Recently, Polytosi et al.<sup>(8)</sup> reported that CO<sub>2</sub> interacting with Rh/Al<sub>2</sub>O<sub>3</sub> dissociates in the presence, but not in the absence, of H<sub>2</sub>. There is disagreement on this point as Iizuki and Tanaka<sup>(9)</sup> find on a similar substrate that CO<sub>2</sub> is dissociated at 300K and moderate CO<sub>2</sub> pressures even in the absence of H<sub>2</sub>.

In this paper, we report the dissociation of CO<sub>2</sub> on both oxidized and reduced samples of Pt/TiO<sub>2</sub>. A discussion of the sites involved in the dissociation of CO<sub>2</sub> as well as those involved in the retention of the reaction products is presented. Previously we have reported that CO<sub>2</sub> is not adsorbed and no carbonate species are formed on reduced TiO<sub>2</sub>.<sup>(10)</sup> Upon exposure of Pt/TiO<sub>2</sub> to CO<sub>2</sub>(g), we have found two kinds of adsorbed linear CO that are attributed to step and terrace sites.<sup>(11)</sup> Here we find that CO<sub>2</sub> dissociation leads to several kinds of carbonate species on TiO<sub>2</sub> and both step and terrace CO species on Pt.

## 2. Experimental.

All the procedures used here were identical to those reported

in another paper from this laboratory.<sup>(11)</sup> Infrared spectra were taken on a Nicolet FT-IR spectrometer and were recorded in absorbance with 2 cm<sup>-1</sup> resolution. Spectra reported here have been corrected by subtraction for absorption of the gas phase, the solid absorbent before adsorption and the CaF<sub>2</sub> windows. All spectra were recorded at room temperature.

Anatase (MCB) was reduced with H<sub>2</sub> at 800°C and soaked in dilute chloroplatinic acid solution to get 2 wt.% Pt/TiO<sub>2</sub>. The sample was dried at 100°C and then washed with distilled water until no chloride could be detected in the wash water. The same procedure has been followed to obtain active catalysts for photoassisted reactions.<sup>(12-16)</sup>

Pellets for IR analysis were pressed between two pieces of paraffin paper; the advantages and disadvantages of this procedure have been discussed previously.<sup>(11)</sup> Each pellet was oxidized at 400°C in the IR cell in order to remove paraffin fragments.

Three kinds of Pt/TiO<sub>2</sub>, each with a different reduction temperature were used in this work. For simplicity each sample is denoted by three temperatures, the oxidation, reduction and evacuation temperatures. For example, the notation 400-200-400 signifies oxidation at 400°C, reduction at 200°C and evacuation at 400°C.

Reactant CO<sub>2</sub> was degassed and purified by pumping through two cold traps maintained at 77 and 195K. These procedures were performed with great care to eliminate any residual CO that might be present in the reactant gas. All interactions of CO<sub>2</sub> with the substrates were carried out at 300K.

### 3. Results and Discussion.

Carbon dioxide adsorption on a 400-200-400 substrate is shown in Fig. 1. When 20 torr of  $\text{CO}_2$  was introduced, Fig. 1a, bands at 2354, 2283, 2077, 1431 and 1245  $\text{cm}^{-1}$  were observed. After 15 min, Fig. 1b, a new band was found at 2092  $\text{cm}^{-1}$ . After 1 hr, Fig. 1c, the 2354  $\text{cm}^{-1}$  band intensity decreased about 10% and the 2077  $\text{cm}^{-1}$  band increased by about a factor of 2. A 23 hr exposure, Fig. 1d, led to an order of magnitude decrease in the intensity of the 2354  $\text{cm}^{-1}$  band and a shift to 2345  $\text{cm}^{-1}$ . In addition, new bands appeared at 1673 and 1617  $\text{cm}^{-1}$  while the intensity of the 2077  $\text{cm}^{-1}$  band increased by a factor of 3. Subsequent evacuation at 20°C for 30 min, Fig. 1e, left only the bands at 2092, 2077 and 1617  $\text{cm}^{-1}$ .

The bands of Fig. 1 are assigned as follows. In accord with the work of Morterra et al.<sup>(17)</sup> and our previous work<sup>(10)</sup>, the 2354 and 2283  $\text{cm}^{-1}$  peaks are assigned to coordinated  $\text{CO}_2$  and  $^{13}\text{CO}_2$  (natural abundance), the 1245 and 1673  $\text{cm}^{-1}$  bands to bidentate carbonate and the 1598 and 1617  $\text{cm}^{-1}$  bands to bicarbonate, respectively. No monodentate carbonate was detected in these experiments.

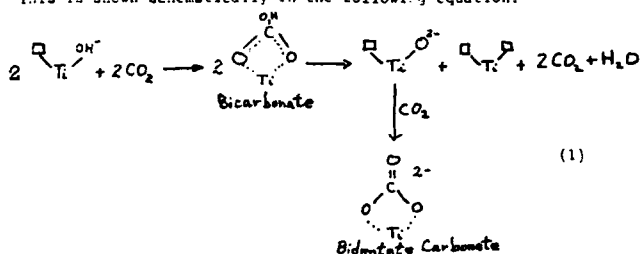
The bands at 2077 and 2092  $\text{cm}^{-1}$  are assigned to linear CO species on step and terrace sites, respectively. (The step-terrace language is used here but the results may be discussed equally well in terms of open and close-packed microcrystallite faces.) These band positions are in excellent agreement with those observed on both reduced and oxidized Pt/TiO<sub>2</sub>.<sup>(11)</sup> The appearance of these two bands and the time

dependence of their development indicates clearly that  $\text{CO}_2$  is dissociating on Pt/TiO<sub>2</sub> and that the product CO occupies terrace sites only after the step sites are filled. It is significant that the absorbance of the 2077  $\text{cm}^{-1}$  peak, Fig. 1e, is 0.05 which is about 25% of that observed at 2094  $\text{cm}^{-1}$  when this substrate is exposed to CO.<sup>(11)</sup> This indicates that the number of adsorbed CO molecules is much larger than could be accounted for on the basis of impurities in the  $\text{CO}_2$ . Additional evidence that the observed CO bands are not due to artifacts, such as CO desorption from the walls, comes from water adsorption experiments where no CO peak was observed.

When this substrate was exposed to CO, a bridged species at 1854  $\text{cm}^{-1}$  was found.<sup>(11)</sup> The fact that it is not found here is ascribed to the relatively low coverage of CO. Hopster and Ibach,<sup>(18)</sup> using high resolution electron energy loss spectroscopy, find that on Pt(111) bridged species appear only at high coverages of CO.

The behavior of the carbonate bands provides insight into the surface processes involving the oxygen atoms formed in the decomposition of carbon dioxide. In the early stages of the reaction, Fig. 1a, b and c, coordinated  $\text{CO}_2$  dominates the spectrum. Some bicarbonate is found along with a hydrogen bonded species involving two adjacent OH groups of bicarbonate species, 3615  $\text{cm}^{-1}$  (not shown here).<sup>(10)</sup> In another paper,<sup>(10)</sup> we show that two interacting bicarbonate species form water and coordinatively unsaturated Ti sites which are active for the formation of bidentate carbonate species in a reaction with  $\text{CO}_2$ .

This is shown schematically in the following equation.

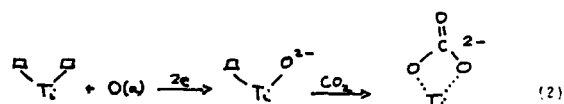


Here  $\square$  represents a vacant coordination site on Ti. These processes are also thought to take place here. While the formation of bidentate carbonate is a convenient way to describe one role played by oxygen atoms formed in the decomposition of  $\text{CO}_2$ , the situation is complicated on 400-200-400 materials since it is not clear whether the oxygen atoms produced in the decomposition process change the surface enough to form bidentate carbonate or whether the reduced sample possesses these sites intrinsically.

To address this question, a 400-400-400 sample was exposed to 20 torr of  $\text{CO}_2$  at 300K. Bidentate carbonate species ( $1674 \text{ cm}^{-1}$ ), bicarbonate ( $1435 \text{ cm}^{-1}$ ), and coordinated  $\text{CO}_2$  ( $2347 \text{ cm}^{-1}$ ) were found after 5 min, Fig. 2a, emphasizing that reduced samples do possess sites for bicarbonate formation. This contrasts to interactions in the absence of Pt where no carbonate species are found.<sup>(10)</sup> With time, 20 min and 2 hr as shown in Fig. 2b and 2c, there were slow changes. After 2 hr, Fig. 2c, the intensity of the coordinated  $\text{CO}_2$  species dropped by a factor of 3 and a small

amount of linear CO appears at  $2056 \text{ cm}^{-1}$  indicating dissociation of  $\text{CO}_2$ .

It is also of interest that, during  $\text{CO}_2$  exposure, the intensity of a broad band in the  $1000\text{--}1200 \text{ cm}^{-1}$  range increased. This is due to Ti-O lattice vibrations and suggests that some of the oxygen atoms derived from the  $\text{CO}_2$  decomposition oxidize the previously reduced  $\text{TiO}_2$  surface. Many papers have dealt with the structure of  $\text{TiO}_2$  following reduction at  $500^\circ\text{C}$  and it is thought to be best described as  $\text{Ti}_4\text{O}_7$ <sup>(19-21)</sup> or  $\text{Ti}_9\text{O}_{17}$ <sup>(22)</sup>. In addition to oxidizing the surface, oxygen atoms can change the surface coordination to lead to bidentate carbonate as follows.



Picking up two electrons corresponds to oxidation of the Ti center.

The very weak intensity of linear CO bands in Fig. 2, as compared to Fig. 1, is related to the strong metal support interaction (SMSI) effect widely discussed in the literature<sup>(23)</sup> and prevailing on strongly reduced Pt/ $\text{TiO}_2$ . In the early stages of the reaction, Fig. 2a, the formation of bidentate carbonate species at  $1674 \text{ cm}^{-1}$  is accompanied by the dissociation of  $\text{CO}_2$ . However, the SMSI effect lowers significantly the chemisorption capacity for CO and very little adsorbed CO accumulates. The decrease of  $1435 \text{ cm}^{-1}$  intensity and the appearance of the water



bending mode at  $1628\text{ cm}^{-1}$  is readily explained by reaction (1).

Figure 3 shows the results of  $\text{CO}_2$  exposure on a 400-N0-400 sample, i.e. oxidized at  $400^\circ\text{C}$  but not reduced. After a 10 min exposure, Fig. 3a, to 20 torr of  $\text{CO}_2$  at  $25^\circ\text{C}$ , bands were observed at 2352, 2284, 1674, 1628, 1597 and  $1434\text{ cm}^{-1}$ . These are assigned to coordinated  $\text{CO}_2$  and  $^{13}\text{CO}_2$ , bidentate carbonate, water and a pair of bands due to bicarbonate, respectively. After 90 min, Fig. 3b, the coordinated  $\text{CO}_2$  intensity ( $2352\text{ cm}^{-1}$ ) dropped by about an order of magnitude while bands due to water ( $1628\text{ cm}^{-1}$ ) and bidentate carbonate ( $1674\text{ cm}^{-1}$ ) doubled. These increases were accompanied by a decrease of the bicarbonate ( $1434\text{ cm}^{-1}$ ) intensity and the relation is understood in terms of reaction (1).

After 3 days, Fig. 3c, the coordinated  $\text{CO}_2$  intensity dropped to a negligible level, a band due to linear CO on Pt appeared at  $2070\text{ cm}^{-1}$ , step sites, the water band at  $1628\text{ cm}^{-1}$  grew and the bicarbonate bands at 1597 and  $1434\text{ cm}^{-1}$  decreased. The slope observed below  $1700\text{ cm}^{-1}$  is attributed to inadequate subtraction.

The slow formation of adsorbed CO species is very interesting. In another paper<sup>(11)</sup> we reported that CO interacted with this kind of support to form  $\text{CO}_2$  and carbonates but the oxygen atoms on step sites were more difficult to remove than those on terrace sites. The results obtained here suggest that some sites are still active for  $\text{CO}_2$  dissociation when the surface is covered with oxygen atoms. However, the reactions are extremely slow. The observed CO frequency,  $2070\text{ cm}^{-1}$ , indicates adsorption at step sites and is consistent with the results of Fig. 1 where step sites are filled before terrace sites.

These experimental results imply that  $\text{CO}_2$  dissociation takes place either on step sites or at the interface between Pt sites and the  $\text{TiO}_2$  support. If the latter occurs then migration of CO to steps must occur subsequently. Such processes are well known on single crystal surfaces.<sup>(24)</sup> Since adsorbed oxygen atoms cover step sites strongly and selectively<sup>(11)</sup> it is difficult to see how CO is selectively adsorbed on step sites. We ascribe  $\text{CO}_2$  dissociation, under all conditions used in this work, to reaction at step sites. This readily accounts for the results of Figs. 1 and 3 where the Pt morphology, non-SMSI, is characterized by rough hemispherical particles with high concentrations of steps and kinks rather than flat particles dominated by Pt(111).<sup>(19)</sup> As noted in the introduction, there is disagreement about whether or not  $\text{CO}_2$  dissociation occurs on Rh samples. Our results point to surface heterogeneity as one possible explanation for this disagreement. Step sites or open faces, present in significant concentrations, could account for the dissociation.

## FIGURE CAPTIONS

Figure 1. CO<sub>2</sub> adsorption at 25°C on a Pt/TiO<sub>2</sub> sample reduced at 200°C (400-200-400). (a)-(d) 20 torr CO<sub>2</sub> exposure for 5 min, 15 min, 1 hr and 23 hr, respectively. (e) Evacuation at 25°C for 30 min after (d).

Figure 2. CO<sub>2</sub> adsorption at 25°C on a Pt/TiO<sub>2</sub> sample reduced at 400°C (400-400-400). (a)-(c) Exposure time of 5 min, 20 min and 2 hr, respectively.

Figure 3. CO<sub>2</sub> adsorption at 25°C on an oxidized Pt/TiO<sub>2</sub> sample (400-NO-400). (a)-(c) Exposure time of 10 min, 90 min and 3 days, respectively.

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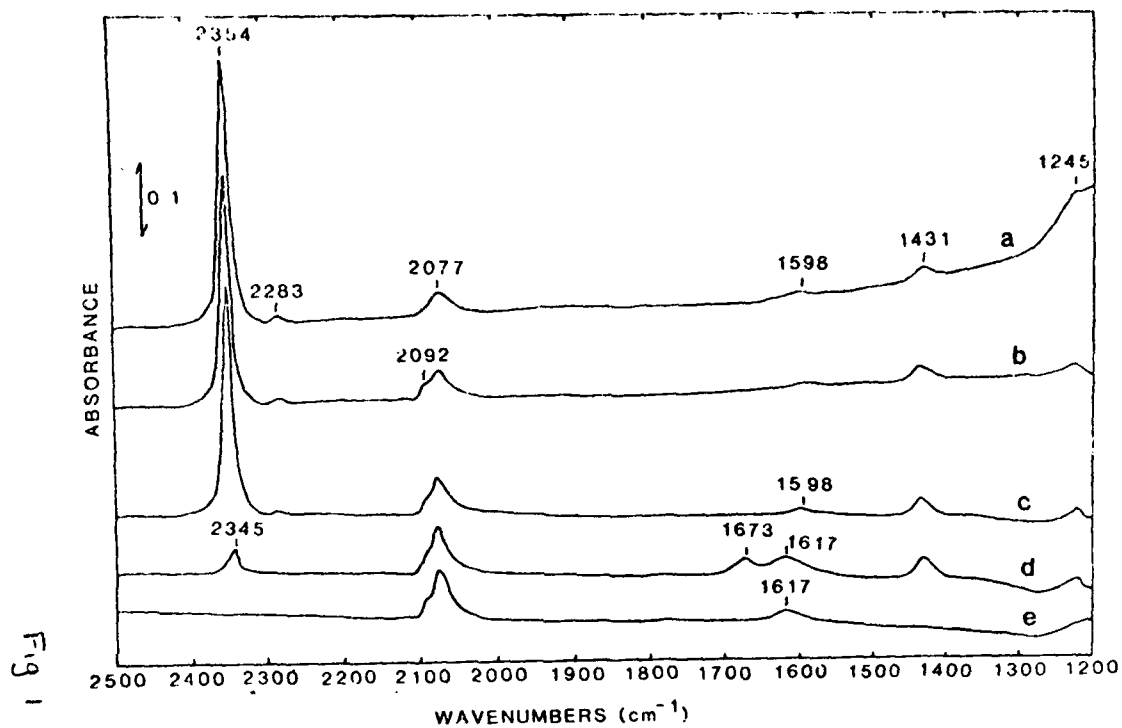
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#### FIGURE CAPTIONS

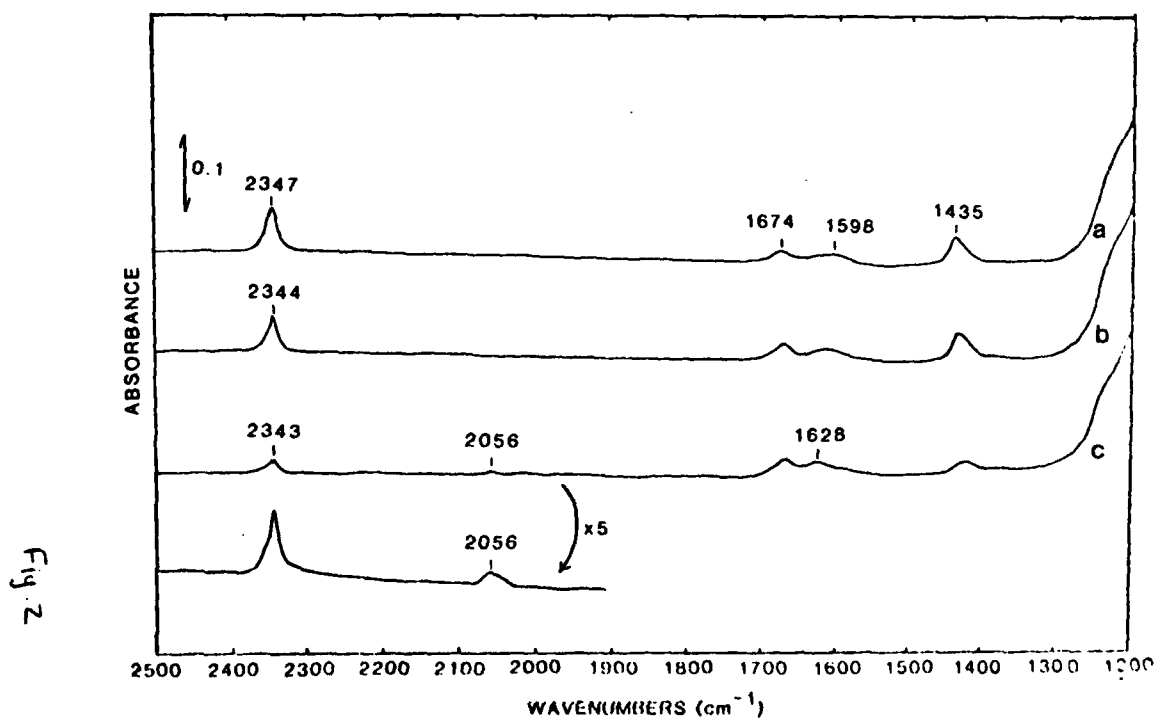
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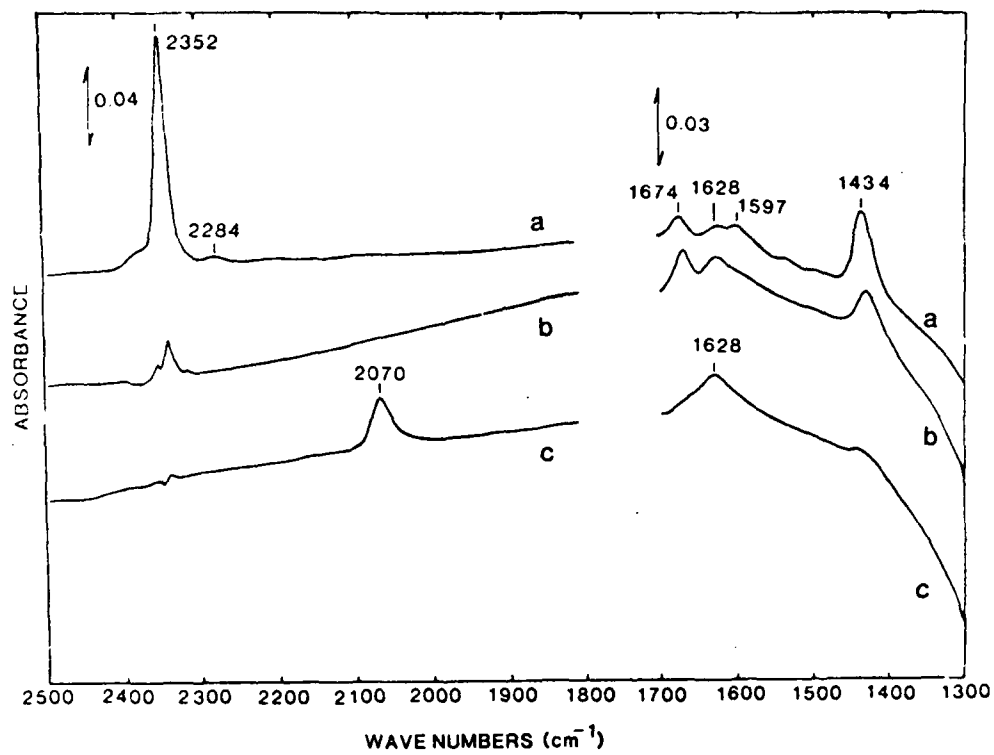
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Figure 3.  $\text{CO}_2$  adsorption at  $25^\circ\text{C}$  on an oxidized  $\text{Pt/TiO}_2$  sample (400-50-400). (a)-(c) Exposure time of 10 min, 90 min and 3 days, respectively.



K. Tanaka and White, Fig. 1





Tonks and White, Fig. 3.

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